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(54) **NANOEMULSIONS COMPRISING AT LEAST ONE AMPHIPHILIC LIPID, AT LEAST ONE OIL, AND AT LEAST ONE NONIONIC POLYMER, AND USES THEREOF**

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(21) **Appl. No.: 09/766,403**(57) **ABSTRACT**

Oil-in-water nanoemulsions comprising oil globules with an average size of less than 150 nm and comprising at least one oil, at least one amphiphilic lipid, and at least one nonionic polymer comprising at least one hydrophobic block and at least one hydrophilic block. Processes comprising such oil-in-water nanoemulsions.

[0031] As examples of nonionic polyether-polyurethanes that can be used in the invention, mention may also be made of the polymer SER-AD FX1100 sold by the company Servo Delden, which comprises an oxyethylene unit and two C_{18} hydrocarbon-based groups at the end of the chain linked to the ethylene oxide via a polyurethane block. Representative nonionic polyether-polyurethanes include Rhéolate 205 comprising a urea function sold by the company RHEOX and Rhéolate 208, 204 and 212, as well as Acrysol RM 184 from the company Rohm & Haas.

[0032] There may also be mentioned the product ELFA-COS T210 comprising a C_{12} -(14) alkyl chain and the product ELFACOS T212 comprising a C_{18} alkyl chain from AKZO.

[0033] The product DW 1206B from RHOM & HMS comprising a C_{20} alkyl chain and with a urethane bond, sold at 20% dry matter content in water, may also be used.

[0034] It is also possible to use solutions and dispersions of these polymers for example in water and for example in an aqueous-alcoholic medium. By way of example of such polymers, there may be mentioned SER-AD FX1010 and SER-AD 1035 sold by the company Hüls, Rhéolate 255, Rhéolate 278 and Rhéolate 244 sold by the company RHEOX. It is also possible to use the products DW 1206F and DW 1206J provided by the company ROHM & HMS.

[0035] Representative polyether-polyurethanes that can be used according to the invention include polyether-polyurethanes described in the article by G. Fonnum, J. Bakke and Fk. Hansen—Colloid Polym. Sci 271, 380-389 (1993), the disclosure of which is incorporated by reference herein.

[0036] Additionally, the at least one nonionic polymer according to the invention can be chosen from:

[0037] (4) copolymers formed from vinylpyrrolidone and at least one hydrophobic monomer comprising at least one fatty chain such as for example:

[0038] the products ANTARON V216 and GANEX V216 (vinylpyrrolidone/hexadecene copolymer) sold by the company I.S.P., and

[0039] the products ANTARON V220 and GANEX V220 (vinylpyrrolidone/eicosene copolymer) sold by the company I.S.P.;

[0040] (5) copolymers formed from at least one C_1 - C_6 alkyl methacrylate and at least one amphiphilic monomer comprising at least one fatty chain and copolymers formed from at least one C_1 - C_6 alkyl acrylate and at least one amphiphilic monomer comprising at least one fatty chain such as for example the oxyethylenated stearyl acrylate/methyl acrylate copolymer sold by the company GOLDSCHMIDT under the name ANTIL 208; and

[0041] (6) copolymers formed from at least one hydrophilic methacrylate and at least one hydrophobic monomer comprising at least one fatty chain and copolymers formed from at least one hydrophilic acrylate and at least one hydrophobic monomer comprising at least one fatty chain, such as, for example, the polyethylene glycol methacrylate/lauryl methacrylate copolymer;

[0042] In the compositions according to the invention, the at least one nonionic polymer comprising at least one hydrophobic block and at least one hydrophilic block is generally present in an amount ranging for example from 0.01% to 10% by weight relative to the total weight of the composition, such as from 0.1% to 5% by weight relative to the total weight of the composition.

[0043] The nanoemulsions according to the present invention can comprise at least one amphiphilic lipid chosen from for example nonionic amphiphilic lipids and anionic amphiphilic lipids.

[0044] The nonionic amphiphilic lipids of the invention can be chosen from, for example:

[0045] 1/-silicone surfactants,

[0046] 2/-nonionic amphiphilic lipids that are fluid at a temperature of less than or equal to 45° C. chosen from esters formed from (i) at least one polyol chosen from polyethylene glycol comprising from 1 to 60 ethylene oxide units, sorbitan, glycerol comprising from 2 to 30 ethylene oxide units, and polyglycerols comprising from 2 to 15 glycerol units, and (ii) at least one fatty acid comprising at least one alkyl chain chosen from saturated and unsaturated, linear and branched C_8 - C_{22} alkyl chains,

[0047] 3/-mixed esters derived from (i) at least one fatty acid, at least one carboxylic acid, and glycerol, and mixed esters derived from (ii) at least one fatty alcohol, at least one carboxylic acid, and glycerol, wherein said at least one carboxylic acid is chosen from α -hydroxy acids and succinic acid,

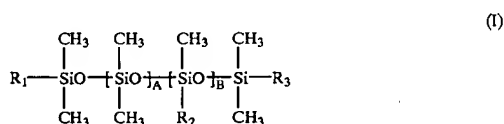
[0048] 4/-fatty acid esters of sugars and fatty alcohol ethers of sugars,

[0049] 5/-surfactants that are solid at a temperature of less than or equal to 45° C. chosen from fatty esters of glycerol, fatty esters of sorbitan, oxyethylenated fatty esters of sorbitan, ethoxylated fatty ethers, and ethoxylated fatty esters, and

[0050] 6/-block copolymers of ethylene oxide (A) and of propylene oxide (B).

[0051] 1/ The silicone surfactants that can be used according to the invention are silicone compounds comprising at least one oxyalkylene chain chosen from oxyethylene $—OCH_2CH_2—$ and oxypropylene $—OCH_2CH_2CH_2—$. Representative silicone surfactants that can be used according to the present invention include silicone surfactants disclosed in U.S. Pat. Nos. 5,364,633 and 5,411,744, the disclosures of which are incorporated by reference herein.

[0052] The silicone surfactants used according to the present invention can be chosen for example from compounds of formula (I):



at a temperature of less than or equal to 45° C., such as esters derived from at least one C₈-C₂₂ fatty acid and at least one sugar chosen from sucrose, maltose, glucose, and fructose, and esters derived from at least one C₁₄-C₂₂ fatty acid and methylglucose.

[0079] The C₈-C₂₂ and C₁₄-C₂₂ fatty acids forming the fatty unit of the esters which can be used in the nanoemulsion of the invention comprise an alkyl chain chosen from saturated and unsaturated linear alkyl chains comprising, respectively, from 8 to 22 and from 14 to 22 carbon atoms. The fatty unit of the esters may be formed for example from stearates, behenates, arachidonates, palmitates, myristates, laurates and caprates. In one embodiment of the invention, stearates for example may be used as the fatty unit.

[0080] As examples of esters of at least one fatty acid and of sucrose, of fatty acids and of maltose, of fatty acids and of glucose, and of fatty acids and of fructose, mention may be made of sucrose monostearate, sucrose distearate and sucrose tristearate and mixtures thereof, such as the products sold by the company Croda under the name Crodesta F50, F70, F110 and F160 having, respectively, an HLB (hydrophilic lipophilic balance) of 5, 7, 11 and 16; and examples of esters of at least one fatty acid and of methylglucose which may be mentioned are methylglucose polyglyceryl-3 distearate, sold by the company Goldschmidt under the name Tego-care 450. Mention may also be made of glucose or maltose monoesters such as methyl o-hexadecanoyl-6-D-glucoside and o-hexadecanoyl-6-D-maltoside.

[0081] The fatty alcohol ethers of sugars, which can be used as surfactants in the nanoemulsion according to the invention, are solid at a temperature of less than or equal to 45° C. and may be chosen for example from ethers of at least one C₈-C₂₂ fatty alcohol and of glucose, of at least one C₈-C₂₂ fatty alcohol and of maltose, of at least one C₈-C₂₂ fatty alcohol and of sucrose, and of at least one C₈-C₂₂ fatty alcohol and of fructose, and ethers of at least one C₁₄-C₂₂ fatty alcohol and of methylglucose. An example of such an ether would include, among other ethers, alkylpolyglucosides.

[0082] The at least one C₈-C₂₂ and the at least one C₁₄-C₂₂ fatty alcohols forming the fatty unit of the ethers which may be used in the nanoemulsion of the invention can comprise at least one alkyl chain chosen from saturated and unsaturated, linear alkyl chains comprising, respectively, from 8 to 22 and from 14 to 22 carbon atoms. The fatty unit of the ethers may be chosen for example from decyl, cetyl, behenyl, arachidyl, stearyl, palmityl, myristyl, lauryl, capryl and hexadecanoyl units, and further such as cetearyl.

[0083] As examples of fatty alcohol ethers of sugars, mention may be made of alkylpolyglucosides such as decylglucoside and laurylglucoside, which is sold, for example, by the company Henkel under the respective names Plantaren 2000 and Plantaren 1200, cetostearyl glucoside optionally as a mixture with cetostearyl alcohol, sold for example, under the name Montanov 68 by the company SEPPIC, under the name Tego-care CG90 by the company Goldschmidt and under the name Emulgade KE3302 by the company Henkel, as well as arachidyl glucoside, for example in the form of a mixture of arachidyl alcohol and behenyl alcohol and arachidyl glucoside, sold under the name Montanov 202 by the company SEPPIC.

[0084] In one embodiment of the invention, the surfactant used can be for example at least one surfactant chosen from sucrose monostearate, sucrose distearate and sucrose tristearate. Additional surfactants that can be used include methylglucose polyglyceryl-3 distearate and alkylpolyglucosides.

[0085] 5/ The fatty esters of glycerol which may be used as surfactants in the nanoemulsion according to the invention, which are solid at a temperature of less than or equal to 45° C., may be chosen for example from esters formed from at least one acid comprising a saturated linear alkyl chain comprising from 16 to 22 carbon atoms and from 1 to 10 glycerol units. One or more of these fatty esters of glycerol may be used in the nanoemulsion of the invention.

[0086] These esters may be chosen for example from stearates, behenates, arachidates and palmitates. In one embodiment, the esters may be chosen for example from stearates and palmitates.

[0087] As examples of surfactants which can be used in the nanoemulsion of the invention, mention may be made of decaglyceryl monostearate, distearate, tristearate and pentastearate (CTFA names: Polyglyceryl-10 stearate, Polyglyceryl-10 distearate, Polyglyceryl-10 tristearate, Polyglyceryl-10 pentastearate), such as the products sold under the respective names Nikkol Decaglyn 1-S, 2-S, 3-S and 5-S by the company Nikko, and diglyceryl monostearate (CTFA name: Polyglyceryl-2 stearate), such as the product sold by the company Nikko under the name Nikkol DGMS.

[0088] The fatty esters of sorbitan which may be used as surfactants in the nanoemulsion according to the invention are solid at a temperature of less than or equal to 45° C. and are chosen from C₁₆-C₂₂ fatty acid esters of sorbitan and oxyethylenated C₁₆-C₂₂ fatty acid esters of sorbitan. They are formed from (i) at least one fatty acid comprising at least one saturated linear alkyl chain comprising, respectively, from 16 to 22 carbon atoms, and from sorbitol, as well as from (ii) at least one fatty acid comprising at least one saturated linear alkyl chain comprising, respectively, from 16 to 22 carbon atoms, and from ethoxylated sorbitol. The oxyethylenated esters generally comprise from 1 to 100 ethylene glycol units, such as from 2 to 40 ethylene oxide (EO) units.

[0089] These esters may be chosen for example from stearates, behenates, and arachidates, palmitates. In one embodiment, the esters may be chosen for example from stearates and palmitates.

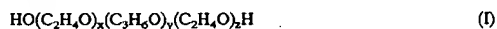
[0090] As examples of surfactants which can be used in the nanoemulsion of the invention, mention may be made of sorbitan monostearate (CTFA name: sorbitan stearate), sold by the company ICI under the name Span 60, sorbitan monopalmitate (CTFA name: sorbitan palmitate), sold by the company ICI under the name Span 40, and sorbitan tristearate 20 EO (CTFA name: Polysorbate 65), sold by the company ICI under the name Tween 65.

[0091] The ethoxylated fatty ethers that are solid at a temperature of less than or equal to 45° C., which may be used as surfactants in the nanoemulsion according to the invention, can be ethers formed from 1 to 100 ethylene oxide units and from at least one fatty alcohol chain comprising from 16 to 22 carbon atoms. The at least one fatty chain of the ethers may be chosen for example from behenyl,

arachidyl, stearyl and cetyl units, and further for example from cetearyl. Examples of ethoxylated fatty ethers which may be mentioned are behenyl alcohol ethers comprising 5, 10, 20 and 30 ethylene oxide units (CTFA names: Beheneth-5, Beheneth-10, Beheneth-20, Beheneth-30), such as the products sold under the names Nikkol BB5, BB10, BB20 and BB30 by the company Nikko, and stearyl alcohol ether comprising 2 ethylene oxide units (CTFA name: steareth-2), such as the product sold under the name Brij 72 by the company ICI.

[0092] The ethoxylated fatty esters that are solid at a temperature of less than or equal to 45° C., which may be used as surfactants in the nanoemulsion according to the invention, are esters formed from 1 to 100 ethylene oxide units and from at least one fatty acid chain comprising from 16 to 22 carbon atoms. The at least one fatty chain in the esters may be chosen for example from stearate, behenate, arachidate and palmitate units. Examples of ethoxylated fatty esters which may be mentioned are the ester of stearic acid comprising 40 ethylene oxide units, such as the product sold under the name Myrj 52 (CTFA name: PEG40 stearate) by the company ICI, as well as the ester of behenic acid comprising 8 ethylene oxide units (CTFA name: PEG-8 behenate), such as the product sold under the name Compritrol HD5 ATO by the company Gattefosse.

[0093] 6/ The block copolymers of ethylene oxide (A) and of propylene oxide (B), which may be used as a surfactant in the nanoemulsion according to the invention, may be chosen for example from at least one block copolymer of formula (I):



[0094] in which x, y, and z, which may be identical or different, are each chosen from integers wherein x+z is an integer ranging from 2 to 100 and y is an integer ranging from 14 to 60, and optionally having an HLB value ranging from 2 to 16.

[0095] The at least one block copolymer of formula (I) may be chosen for example from poloxamers, such as Poloxamer 231, and further such as the product sold by the company ICI under the name PLURONIC L81, which corresponds to the block copolymer of formula (i) wherein x=z=6, y=39 (HLB 2); Poloxamer 282, such as the product sold by the company ICI under the name PLURONIC L92, which corresponds to the block copolymer of formula (I) wherein x=z=10, y=47 (HLB 6); and Poloxamer 124, such as the product sold by the company ICI under the name PLURONIC L44, which corresponds to the block copolymer of formula (I) wherein x=z=11, y=21 (HLB 16).

[0096] Representative nonionic amphiphilic lipids that can be used for example are chosen from:

[0097] polyethylene glycol isostearate (8 mol of ethylene oxide),

[0098] diglyceryl isostearate,

[0099] polyglyceryl monolaurate, polyglyceryl monostearate, and polyglyceryl distearate which comprise 10 glycerol units,

[0100] sorbitan oleate, and

[0101] sorbitan isostearate.

[0102] Representative anionic amphiphilic lipids of the invention, for example, can be chosen from:

[0103] alkyl ether citrates,

[0104] alkoxyated alkenyl succinates, alkoxyated glucose alkenyl succinates, and

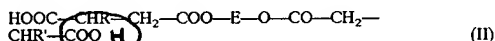
[0105] alkoxyated methylglucose alkenyl succinates.

[0106] The alkyl ether citrates which may be used as surfactants in the nanoemulsion according to the invention may be chosen for example from at least one alkyl ether citrate chosen from monoesters, diesters, and triesters formed from citric acid and from at least one oxyethylenated fatty alcohol comprising at least one alkyl chain chosen from linear and branched, saturated and unsaturated alkyl chains comprising from 8 to 22 carbon atoms, and comprising from 3 to 9 ethoxylated groups. One embodiment of the invention may comprise at least one of the above-mentioned citrates in the nanoemulsion. Another embodiment may comprise at least two of the above-mentioned citrates in the nanoemulsion.

[0107] These citrates may be chosen, for example, from the monoesters, diesters, and triesters of citric acid and of ethoxylated lauryl alcohol, comprising from 3 to 9 ethoxylated groups, which are, for example, sold by the company Witco under the name WITCONOL EC. For example, WITCONOL EC 2129, which is predominantly a dilaureth-9 citrate, and Witconol EC 3129, which is predominantly a trilaureth-9 citrate, can be chosen.

[0108] When used, the alkyl ether citrates used as surfactants can for example be neutralized to a pH of about 7 with at least one base chosen from inorganic bases (such as sodium hydroxide, potassium hydroxide and ammonia) and organic bases (such as mono-ethanolamine, diethanolamine, triethanolamine, 1,3-aminomethylpropanediol, N-methylglucamine and basic amino acids like arginine and lysine).

[0109] The alkenyl succinates which may be used as surfactants in the nanoemulsion of the invention can, for example, be chosen from alkoxyated alkenyl succinates, alkoxyated glucose alkenyl succinates, and alkoxyated methylglucose alkenyl succinates that correspond to compounds of formulae (I) and (II):



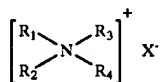
[0110] in which:

[0111] R and R', which may be identical or different, are each chosen from linear and branched alkenyl groups comprising from 6 to 22 carbon atoms,

[0112] E is chosen from oxyethylene chains of formula $(\text{C}_2\text{H}_4\text{O})_n$ in which n is chosen from integers ranging from 2 to 100, oxypropylene chains of formula $(\text{C}_3\text{H}_6\text{O})_{n'}$ in which n' is chosen from integers ranging from 2 to 100, and random and block copolymers comprising chains chosen from oxyethylene chains of formula $(\text{C}_2\text{H}_4\text{O})_n$ and oxypropylene chains of formula $(\text{C}_3\text{H}_6\text{O})_{n'}$ (such as oxyethylenated glucose copolymers, oxyethylenated methylglucose copolymers, oxypropylenated glucose copolymers, and oxypropylenated methylglucose copolymers) such that:

[0135] The quaternary ammonium salts are, for example, chosen from:

[0136] A) quaternary ammonium salts of formula (IV) below:

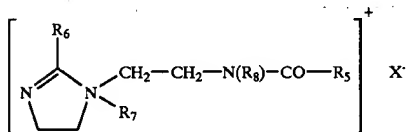


[0137] in which:

[0138] R_1 , R_2 , R_3 , and R_4 , which may be identical or different, are each chosen from linear and branched aliphatic groups comprising from 1 to 30 carbon atoms, and aromatic groups, such as aryl and alkylaryl groups. The aliphatic groups can comprise hetero atoms, such as oxygen, nitrogen, and sulfur, and halogens. And the aliphatic groups can be chosen, for example, from alkyl, alkoxy, polyoxy(C_2 - C_6)alkylene, alkylamide, $(C_2$ - $C_{22})$ alkylamido(C_2 - C_6)alkyl, $(C_{12}$ - $C_{22})$ alkylacetate, and hydroxyalkyl groups comprising from 1 to 30 carbon atoms;

[0139] X^- is an anion chosen from halides, phosphates, acetates, lactates, $(C_2$ - C_6)alkyl sulfates, alkyl sulfonates, and alkylaryl sulfonates;

[0140] B) quaternary ammonium salts of imidazolium, such as, for example, the salts of formula (V) below:



[0141] in which:

[0142] R_5 is chosen from alkenyl and alkyl groups comprising from 8 to 30 carbon atoms, for example groups derived from tallow fatty acid,

[0143] R_6 is chosen from a hydrogen atom, C_1 - C_4 alkyl groups, and alkenyl and alkyl groups comprising from 8 to 30 carbon atoms,

[0144] R_7 is chosen from C_1 - C_4 alkyl groups,

[0145] R_8 is chosen from a hydrogen atom and C_1 - C_4 alkyl groups,

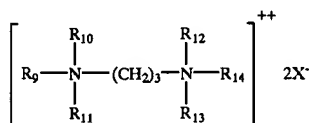
[0146] X^- is an anion chosen from halides, phosphates, acetates, lactates, alkyl sulfates, alkyl sulfonates, and alkylaryl sulfonates.

[0147] In one embodiment, for example, R_5 and R_6 are chosen from alkenyl and alkyl groups comprising from 12 to 21 carbon atoms, for example, alkenyl and alkyl groups derived from tallow fatty acid, and wherein said R_5 and R_6 are chosen such that said quaternary ammonium salts of imidazolium comprise at least one alkenyl group and at

least one alkyl group, R_7 is methyl, and R_8 is hydrogen. Such products are, for example, (1) Quaternium-27 (International Cosmetic Ingredient Dictionary and Handbook, hereafter "CTFA", 1997), i.e., "Rewoquat" W75, W75PG, and W90, and (2) Quaternium-83 (CTFA 1997), i.e., "Rewoquat" W75HPG, which are sold by the company Witco.

[0148] Additionally, the quaternary ammonium salts are, for example, chosen from:

[0149] C) diquaternary ammonium salts of formula (VI):



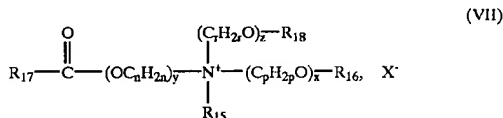
[0150] in which:

[0151] R_9 is chosen from aliphatic groups comprising from 16 to 30 carbon atoms,

[0152] R_{10} , R_{11} , R_{12} , R_{13} and R_{14} , which may be identical or different, are each chosen from a hydrogen atom and alkyl groups comprising from 1 to 4 carbon atoms, and

[0153] X^- is an anion chosen from halides, acetates, phosphates, nitrates and methyl sulfates. For example, such diquaternary ammonium salts can comprise propane tallow diammonium dichloride.

[0154] D) Quaternary ammonium salts comprising at least one ester function. The quaternary ammonium salts comprising at least one ester function that can be used according to the invention are, for example, those of formula (VII) below:

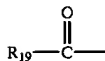


[0155] in which:

[0156] R_{15} is chosen from C_1 - C_6 alkyl groups, C_1 - C_6 hydroxyalkyl groups and C_1 - C_6 dihydroxyalkyl groups;

[0157] R_{16} is chosen from:

[0158] acyl groups of the following formula:



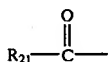
[0159] wherein R_{19} is defined below,

[0160] linear and branched, saturated and unsaturated, C_1 - C_{22} hydrocarbon-based groups, and

[0161] a hydrogen atom;

[0162] R_{18} is chosen from:

[0163] acyl groups of the following formula:



[0164] wherein R_{21} is defined below,

[0165] linear and branched, saturated and unsaturated, C_1 - C_6 hydrocarbon-based groups, and

[0166] a hydrogen atom;

[0167] R_{17} , R_{19} and R_{21} , which may be identical or different, are each chosen from linear and branched, saturated and unsaturated, C_1 - C_{21} , hydrocarbon-based groups;

[0168] n , p and r , which may be identical or different, are each chosen from integers ranging from 2 to 6;

[0169] y is chosen from integers ranging from 1 to 10;

[0170] x and z , which may be identical or different, are each chosen from integers ranging from 0 to 10;

[0171] X^- is chosen from simple and complex, organic and inorganic anions;

[0172] provided that the sum $x+y+z$ is from 1 to 15, and that when x is 0, then R_{16} is chosen from linear and branched, saturated and unsaturated, C_1 - C_{22} hydrocarbon-based groups, and that when z is 0, then R_{18} is chosen from linear and branched, saturated and unsaturated, C_1 - C_6 hydrocarbon-based groups.

[0173] In one embodiment, the R_{15} alkyl groups may be linear or branched and further, for example, linear.

[0174] For example, R_{15} may be chosen from methyl, ethyl, hydroxyethyl and dihydroxypropyl groups and further for example from methyl and ethyl groups.

[0175] The sum $x+y+z$ may for example range from 1 to 10.

[0176] When R_{16} is chosen from linear and branched, saturated and unsaturated, C_1 - C_{22} hydrocarbon-based groups, R_{16} may be long and comprise from 12 to 22 carbon atoms, or short and comprise from 1 to 3 carbon atoms.

[0177] When R_{18} is chosen from linear and branched, saturated and unsaturated, C_1 - C_6 hydrocarbon-based groups, R_{18} may for example comprise from 1 to 3 carbon atoms.

[0178] R_{17} , R_{19} , and R_{21} , which may be identical or different, can each, for example, be chosen from linear and branched, saturated and unsaturated, C_1 - C_{21} hydrocarbon-based groups, and for example from linear and branched, saturated and unsaturated, C_{11} - C_{21} , alkyl and alkenyl groups.

[0179] x and z , which may be identical or different, can for example each be chosen from 0 or 1.

[0180] y for example may be equal to 1.

[0181] n , p and r , which may be identical or different, can for example each be chosen from 2 and 3 and in one embodiment equal to 2.

[0182] The anion for example can be chosen from halides (chloride, bromide, and iodide) and alkyl sulfates, such as methyl sulfate. However, methanesulfonate, phosphate, nitrate, tosylate, anions derived from organic acids, such as acetate and lactate, and any other anions compatible with the ammonium comprising an ester function, may be used.

[0183] As a further example, the anion X^- can be chosen from chloride and methyl sulfate.

[0184] Further examples of ammonium salts of formula (VII) are those in which:

[0185] R_{15} is chosen from methyl and ethyl groups,

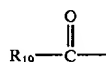
[0186] x and y are equal to 1;

[0187] z is equal to 0 or 1;

[0188] n , p and r are equal to 2;

[0189] R_{16} is chosen from:

[0190] acyl groups:



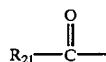
[0191] wherein R_{19} is defined below,

[0192] methyl, ethyl and C_{14} - C_{22} hydrocarbon-based groups, and

[0193] a hydrogen atom;

[0194] R_{18} is chosen from:

[0195] acyl groups:



[0196] wherein R_{21} is defined below,

[0197] a hydrogen atom;

[0198] R_{17} , R_{19} and R_{21} , which may be identical or different, are each chosen from linear and branched, saturated and unsaturated, C_{13} - C_{17} hydrocarbon-based groups, such as from linear and branched, saturated and unsaturated C_{13} - C_{17} alkyl and alkenyl groups.

[0199] The hydrocarbon-based groups can for example be linear.

[0200] Representative compounds of formula (VII) are chosen from diacyloxyethylmethylammonium, diacyloxyethylhydroxyethylmethylammonium, monoacyloxyethylhydroxyethylmethylammonium, triacyloxyethylmethylammonium and monoacyloxyethylhydroxyethylmethylammonium salts

(for example chloride and methyl sulfate). The acyl groups can for example comprise from 14 to 18 carbon atoms and can for example be obtained from plant oils, such as palm oil and sunflower oil. When the compound comprises several acyl groups, these groups, which may be independently chosen, may independently be identical or different.

[0201] These products are obtained, for example, by direct esterification of compounds chosen from triethanolamine, triisopropanolamine, alkyldiethanolamines and alkyldiisopropanolamines, which are optionally oxyalkylenated, with fatty acids or with fatty acid mixtures of plant or animal origin, and by transesterification of the methyl esters thereof. This esterification is followed by a quaternization using an alkylating agent such as alkyl halides (such as methyl and ethyl halides), dialkyl sulfates (for example dimethyl and diethyl sulfates), methyl methanesulfonate, methyl paratoluenesulfonate, glycol chlorohydrin and glycerol chlorohydrin.

[0202] Such compounds are sold, for example, under the names Dehyquart by the company Henkel, Stepanquat by the company Stepan, Noxamium by the company Ceca and Rewoquat WE 18 by the company Rewo-Witco.

[0203] One embodiment of the invention can comprise at least one quaternary ammonium monoester salt, at least one quaternary ammonium diester salt, and at least one quaternary ammonium triester salt, wherein said quaternary ammonium diester salt is, for example, present in a majority by weight.

[0204] Such an embodiment may comprise, for example, 15% to 30% by weight of acyloxyethylhydroxyethylmethylammonium methyl sulfate, 45% to 60% by weight of diacyloxyethylhydroxyethylmethylammonium methyl sulfate, and 15% to 30% by weight of triacyloxyethylmethylammonium methyl sulfate, wherein said acyl groups comprise from 14 to 18 carbon atoms, and wherein said acyl groups are derived from palm oil that is optionally partially hydrogenated.

[0205] It is also possible to use the ammonium salts comprising at least one ester function, described in U.S. Pat. Nos. 4,874,554 and 4,137,180, the disclosures of which are incorporated by reference herein.

[0206] Representative quaternary ammonium salts of formula (IV) include tetraalkylammonium chlorides such as, for example, dialkyldimethylammonium chlorides and alkyltrimethylammonium chlorides, in which the alkyl group comprises from 12 to 22 carbon atoms, for example behenyltrimethylammonium chloride, distearyltrimethylammonium chloride, cetyltrimethylammonium chloride, and benzyltrimethylammonium chloride, and stearamidopropyltrimethylammonium acetate, and stearamidopropyltrimethylammonium chloride sold under the name "Cepharyl 70" by the company Van Dyk.

[0207] According to one embodiment of the invention, the quaternary ammonium salt can be behenyltrimethylammonium chloride.

[0208] The at least one additional ionic amphiphilic lipid chosen from cationic amphiphilic lipids and anionic amphiphilic lipids is generally present in the nanoemulsion of the invention in an amount ranging for example from 0.01% to 10% by weight relative to the total weight of the nanoemulsion, such as for example from 0.2% to 5% by weight relative to the total weight of the nanoemulsion.

[0209] The at least one oil that may be used in the nanoemulsion of the invention is, for example, chosen from:

[0210] animal and plant oils formed by fatty acid esters of polyols, such as liquid triglycerides, for example sunflower oil, corn oil, soybean oil, avocado oil, jojoba oil, marrow oil, grapeseed oil, sesame oil, hazelnut oil, fish oils, glyceryl tricaproate, and plant and animal oils of formula R_9COOR_{10} in which R_9 is chosen from fatty acid residues comprising from 7 to 29 carbon atoms and R_{10} is chosen from linear and branched hydrocarbon-based chains comprising from 3 to 30 carbon atoms, such as alkyl and alkenyl, for example, purcellin oil and liquid jojoba wax;

[0211] natural and synthetic essential oils such as, for example, eucalyptus oil, lavandin oil, lavender oil, vetiver oil, Litsea cubeba oil, lemon oil, sandalwood oil, rosemary oil, camomile oil, savory oil, nutmeg oil, cinnamon oil, hyssop oil, caraway oil, orange oil, geraniol oil, cade oil and bergamot oil;

[0212] synthetic oils;

[0213] mineral oils such as hexadecane and liquid paraffin;

[0214] halogenated oils, such as fluorocarbons, for example, fluoroamines (including for example perfluorotributylamine), fluorohydrocarbons (including for example perfluorodecahydro-naphthalene), fluoroesters and fluoroethers;

[0215] esters of at least one mineral acid and of at least one alcohol;

[0216] liquid carboxylic acid esters; and

[0217] volatile and non-volatile silicone oils.

[0218] Volatile and non-volatile silicone oils can for example be used in the presence of at least one non-silicon oil (oil which does not contain silicon atom). When used, the total amount of such silicone oils is generally an amount ranging for example from 5% to 50% by weight relative to the total weight of oils.

[0219] The synthetic oils can be chosen from for example polyolefins, such as poly- α -olefins and further such as:

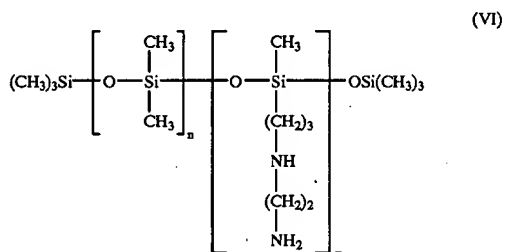
[0220] poly- α -olefins chosen from hydrogenated and non-hydrogenated polybutene poly- α -olefins, such as hydrogenated and non-hydrogenated polyisobutene poly- α -olefins.

[0221] One embodiment may comprise at least one isobutylene oligomer with a molecular weight of less than 1000 and at least one polyisobutylene with a molecular weight of greater than 1000 such as for example ranging from 1000 to 15000.

[0222] Representative carboxylic acid esters include monocarboxylic acid esters, dicarboxylic acid esters, tricarboxylic acid esters, and tetracarboxylic acid esters. The total number of carbons in the esters is generally equal to 10 or more, such as less than 100 and further such as less than 80.

[0223] The monocarboxylic acid esters can be chosen from saturated and unsaturated, linear and branched C_1 - C_{26} aliphatic acid monoesters derived from alcohols chosen from saturated and unsaturated, linear and branched C_1 - C_{26} aliphatic alcohols, wherein the total number of carbons in the esters is generally equal to 10 or more.

[0248] One aminosilicone of said at least one aminosilicone corresponding to formula (V) is known as "trimethylsilylamodimethicone" of formula (VI):



[0249] in which:

[0250] m and n are numbers such that the sum (n+m) can range for example from 1 to 2000, such as for example from 50 to 150, wherein n can be for example chosen from numbers ranging from 0 to 1999, such as for example from 49 to 149, and

[0257] R_6 is chosen from divalent hydrocarbon-based groups, such as divalent C_1 - C_{18} alkylene groups and divalent C_1 - C_{18} alkyleneoxy groups, for example C_1 - C_8 alkyleneoxy groups, wherein said R_6 is bonded to the Si by way of an SiC bond;

[0258] Q^- is an anion that can be for example chosen from halide ions, such as chloride, and organic acid salts (such as acetate);

[0259] r is an average statistical value ranging from 2 to 20, such as from 2 to 8;

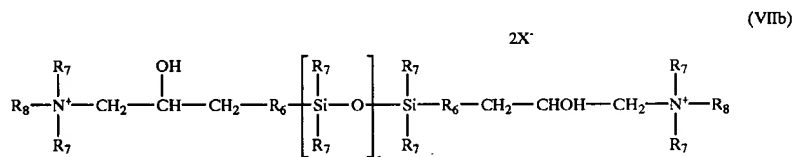
[0260] s is an average statistical value ranging from 20 to 200, such as from 20 to 50.

[0261] Such aminosilicones are described more particularly in U.S. Pat. No. 4,185,087, the disclosure of which is incorporated by reference herein.

[0262] A silicone which falls within this class is the silicone sold by the company Union Carbide under the name "Ucar Silicone ALE 56".

[0263] Further examples of said at least one aminosilicone include:

[0264] d) quaternary ammonium silicones of formula (VIIb):

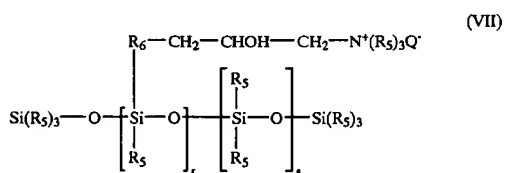


[0251] wherein m can be chosen from numbers ranging for example from 1 to 2000, such as for example from 1 to 10.

[0252] Such polymers are described, for example in patent application EP-A-95238, the disclosure of which is incorporated herein by reference.

[0253] Additional said at least one aminosilicone of the invention include:

[0254] (c) said at least one aminosilicone of formula (VII):



[0255] in which:

[0256] R_5 is chosen from monovalent hydrocarbon-based groups comprising from 1 to 18 carbon atoms, such as C_1 - C_{18} alkyl groups and C_2 - C_{18} alkenyl groups, for example methyl;

[0265] in which:

[0266] groups R_7 , which may be identical or different, are each chosen from monovalent hydrocarbon-based groups comprising from 1 to 18 carbon atoms, such as C_1 - C_{18} alkyl groups, for example methyl, C_2 - C_{18} alkenyl groups, and rings comprising 5 or 6 carbon atoms;

[0267] R_6 is chosen from divalent hydrocarbon-based groups, such as divalent C_1 - C_{18} alkylene groups and divalent C_1 - C_{18} alkyleneoxy, for example C_1 - C_8 , group connected to the Si by an SiC bond;

[0268] R_8 , which may be identical or different, represent a hydrogen atom, a monovalent hydrocarbon-based group comprising from 1 to 18 carbon atoms, and in particular a C_1 - C_{18} alkyl group, a C_2 - C_{18} alkenyl group or a group $-R_6-NHCOR_7$;

[0269] X^- is an anion such as a halide ion, in particular chloride, or an organic acid salt (acetate, etc.);

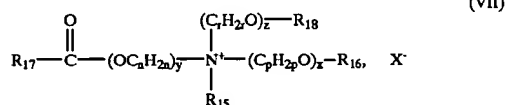
[0270] r represents an average statistical value from 2 to 200, such as for example from 5 to 100.

[0271] Such silicones are described, for example, in application EP-A-0 530 974, the disclosure of which is incorporated by reference herein.

R_{10} , R_{11} , R_{12} , R_{13} and R_{14} , which may be identical or different, are each chosen from a hydrogen atom and alkyl groups comprising from 1 to 4 carbon atoms, and

X^- is an anion chosen from halides, acetates, phosphates, nitrates and methyl sulfates; and

D) quaternary ammonium salts comprising at least one ester function chosen from said quaternary ammonium salts of formula (VII):

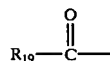


in which:

R_{15} is chosen from C_1 - C_6 alkyl groups, C_1 - C_6 hydroxy-alkyl groups and C_1 - C_6 dihydroxyalkyl groups;

R_{16} is chosen from:

acyl groups of the following formula:



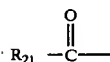
wherein R_{19} is defined below,

linear and branched, saturated and unsaturated, C_1 - C_{22} hydrocarbon-based groups, and

a hydrogen atom;

R_{18} is chosen from:

acyl groups of the following formula:



wherein R_{21} is defined below,

linear and branched, saturated and unsaturated, C_1 - C_6 hydrocarbon-based groups, and

a hydrogen atom;

R_{17} , R_{19} , and R_{21} , which may be identical or different, are each chosen from linear and branched, saturated and unsaturated, C_7 - C_{21} , hydrocarbon-based groups;

n , p and r , which may be identical or different, are each chosen from integers ranging from 2 to 6;

y is chosen from integers ranging from 1 to 10;

x and z , which may be identical or different, are each chosen from integers ranging from 0 to 10;

X^- is chosen from simple and complex, organic and inorganic anions; and

provided that the sum $x+y+z$ is from 1 to 15, and that when x is 0, then R_{16} is chosen from linear and branched, saturated and unsaturated, C_1 - C_{22} hydrocarbon-based groups, and that when z is 0, then R_{18} is chosen from linear and branched, saturated and unsaturated, C_1 - C_6 hydrocarbon-based groups.

31. A nanoemulsion according to claim 30, wherein said aromatic groups are chosen from aryl and alkylaryl groups.

32. A nanoemulsion according to claim 30, wherein said hetero atoms are chosen from oxygen, nitrogen, and sulfur.

33. A nanoemulsion according to claim 30, wherein said aliphatic groups are chosen from alkyl, alkoxy, polyoxy(C_2 - C_6)alkylene, alkylamide, (C_{12} - C_{22})alkylamido(C_2 - C_6)alkyl, (C_{12} - C_{22})alkylacetate, and hydroxyalkyl groups comprising from 1 to 30 carbon atoms.

34. A nanoemulsion according to claim 30, wherein said alkenyl and alkyl groups comprising from 8 to 30 carbon atoms are chosen from groups derived from tallow fatty acid.

35. A nanoemulsion according to claim 30, wherein said diquaternary ammonium salts of formula (VI) comprise propane tallow diammonium dichloride.

36. A nanoemulsion according to claim 30, wherein said R_{15} alkyl groups are chosen from linear and branched alkyl groups.

37. A nanoemulsion according to claim 36, wherein said R_{15} alkyl groups are chosen from linear alkyl groups.

38. A nanoemulsion according to claim 37, wherein said R_{15} alkyl groups are chosen from methyl, ethyl, hydroxy-ethyl and dihydroxypropyl groups.

39. A nanoemulsion according to claim 38, wherein said R_{15} alkyl groups are chosen from methyl and ethyl groups.

40. A nanoemulsion according to claim 30, wherein said sum of $x+y+z$ ranges from 1 to 10.

41. A nanoemulsion according to claim 30, wherein when said R_{16} is chosen from linear and branched, saturated and unsaturated, C_1 - C_{22} hydrocarbon-based groups, R_{16} is chosen from hydrocarbon-based groups comprising from 12 to 22 carbon atoms, and hydrocarbon-based groups comprising from 1 to 3 carbon atoms.

42. A nanoemulsion according to claim 30, wherein when said R_{18} is chosen from linear and branched, saturated and unsaturated, C_1 - C_6 hydrocarbon-based groups, R_{18} comprises from 1 to 3 carbon atoms.

43. A nanoemulsion according to claim 42, wherein said R_{18} comprises from 1 to 3 carbon atoms.

44. A nanoemulsion according to claim 30, wherein said R_{17} , R_{19} and R_{21} , which may be identical or different, are each chosen from linear and branched, saturated and unsaturated C_{11} - C_{21} , hydrocarbon-based groups.

45. A nanoemulsion according to claim 44, wherein said R_{17} , R_{19} and R_{21} , which may be identical or different, are each chosen from linear and branched, saturated and unsaturated, C_{11} - C_{21} alkyl and alkenyl groups.

46. A nanoemulsion according to claim 30, wherein said x and z , which may be identical or different, are each chosen from 0 or 1.

47. A nanoemulsion according to claim 30, wherein said y is equal to 1.

48. A nanoemulsion according to claim 30, wherein said n , p and r , which may be identical or different, are each chosen from 2 and 3.